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(22)Date of filing : 18.06.1998 (72)Inventor : ISHII YOSHITO
YOKOBORI KENJI
KAMI TAKESHI
NISHIDA TATSUYA
TAKEI KOICHI
FUJITA ATSUSHI

(54) GRAPHITE PARTICLE AND MANUFACTURE THEREFOR, NEGATIVE ELECTRODE CARBON MATERIAL FOR LITHIUM SECONDARY BATTERY, NEGATIVE ELECTRODE FOR THE LITHIUM SECONDARY BATTERY, AND LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide particles suitable for a negative electrode carbon material for a lithium secondary battery of high capacity by firing and graphitizing a mixture, including a graphitizable material and at least two kinds of compounds which include different metallic elements.

SOLUTION: A mixture comprising a graphitizable material, a compound including B element, and a compound including at least one kind of elements of Fe, Si, Ni, and Ti, is fired and graphitized. Here, with respect of irreversible capacity at the first cycle of a lithium secondary battery manufactured, it is desirable for the amount of the compound including the B element to be in the range of 0.05 to 5 wt.% in terms of the B element relative to the total amount of the graphitizable material and the compounds including metallic elements, more preferable to range from 0.05 to 3 wt.%, and still more preferable to range from 0.05 to 1 wt.%. It is preferable for the amount of the

compound added including at least one kind of elements of Fe, Si, Ni, and Ti, to be in the range of 0.1 to 30 wt.% in terms of each element, and is especially desirable to be in the range of 0.5 to 5 wt.%.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacturing method of the graphite particle characterized by including the process which calcinates and graphitizes the mixture containing the ingredient which can be graphitized, and at least two kinds of compounds containing a different metallic element.

[Claim 2] The manufacturing method of the graphite particle according to claim 1 which is the compound with which one of at least two kinds of compounds containing a different metallic element contains B element.

[Claim 3] The manufacturing method of the graphite particle according to claim 1 at least two kinds of whose compounds containing a different metallic element are a compound containing B element, and a compound containing at least one kind of element of Fe, Si, nickel, and Ti.

[Claim 4] The manufacturing method of the graphite particle according to claim 3 which is 0.1 - 30 % of the weight in element conversion to the total quantity of the ingredient which the amount of the compound which is 0.05 - 5 % of the weight in B element conversion, and contains at least one kind of element of Fe, Si, nickel, and Ti to the total quantity of the ingredient which the amount of the compound containing B element can graphitize, and the compound containing a metallic element can graphitize, and the compound containing a metallic element.

[Claim 5] The manufacturing method of the graphite particle according to claim 1, 2, 3, or 4 which is that in which the ingredient which can be graphitized contains the carbonaceous powder whose mean diameter is 1-50 micrometers, and the binder which can be graphitized.

[Claim 6] The graphite particle containing at least two kinds of different metallic elements.

[Claim 7] The graphite particle according to claim 6 in which a metallic element contains B element and at least one kind of element of Fe, Si, nickel, and Ti.

[Claim 8] The graphite particle according to claim 6 or 7 whose content of a metallic element is 0.01 - 5 % of the weight.

[Claim 9] The graphite particle according to claim 6, 7, or 8 below 8m²/g and whose aspect ratio 10-100 micrometers and specific surface area are [the distance d between layers of a crystal (002) / the microcrystal size L_c (002) of 3.38Å or less and C shaft orientations] 1.1-5 for 500Å or more and mean particle diameter.

[Claim 10] The negative-electrode carbon material for lithium secondary batteries which consists of a graphite particle obtained according to one of manufacturing methods according to claim 1 to 4, or a graphite particle according to claim 5 to 9.

[Claim 11] The negative electrode for lithium secondary batteries which applies a carbon material according to claim 10 to a charge collector, and it comes to unify.

[Claim 12] The lithium secondary battery which comes to have a negative electrode according to claim 11 and a positive electrode containing a lithium compound.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a graphite particle, its manufacturing method, the negative-electrode carbon material for lithium secondary batteries, the negative electrode for lithium secondary batteries, and a lithium secondary battery. It is related with the negative-electrode carbon material for obtaining it in the lithium secondary battery suitable in more detail and negative-electrode list suitable in more detail which are high capacity and were excellent in the cycle property using for a portable device, an electric vehicle, stationary energy storage, etc., a graphite particle, and its manufacturing method.

[0002]

[Description of the Prior Art] The artificial-graphite particle which graphitized for example, a natural-graphite particle, the artificial-graphite particle which graphitized corks, organic system polymeric materials, a pitch, etc., the graphite particle which ground these are used for the negative-electrode material of the conventional lithium secondary battery. It mixes with an organic system binder and an organic solvent, and these graphite particles are considered as a graphite paste, apply this graphite paste on the surface of copper foil, dry a solvent, and are used as a negative electrode for lithium secondary batteries. For example, as shown in JP,62-23433,B, the problem of the contents short circuit by the dendrite of a lithium is solved by using a graphite for a negative electrode, and amelioration of a cycle property is aimed at.

[0003] However, since it is weak compared with association of the direction of a field of a crystal, by grinding, the bonding strength between the layers of the crystal of C shaft orientations goes out, and, as for the natural graphite with which the graphite crystal is developed, association between graphite layers serves as the so-called lepidic form graphite particle with a large aspect ratio. Since the aspect ratio of flaky graphite is large, when it kneads with a binder, it applies to a charge collector and an electrode is produced, the destruction inside an electrode arises by expansion and contraction of C shaft orientations in which a flaky graphite particle carries out orientation in the direction of a field of a charge collector consequently which charge-and-discharge capacity and a rapid charge-and-discharge property not only tend to fall, but it generates by the repeat of the occlusion and emission of the lithium to a graphite crystal, and it has the problem to which a cycle property falls.

[0004] On the other hand, although an aspect ratio can make small comparatively the artificial graphite which calcinated corks, the pitch, the organic system ingredient, etc. above 2000 degrees C compared with a natural graphite, since development of a graphite crystal is bad, charge-and-discharge capacity is low. The crystallinity is raised by calcinating with a graphitization catalyst, and an artificial graphite can raise charge-and-discharge capacity.

However, if the crystallinity of an artificial graphite is raised, the edge of a graphite crystal will become easy to increase on the front face of an artificial-graphite particle. The edge of the crystal of an artificial-graphite particle front face has the problem on which it is easy to react with the electrolytic solution to, and the cycle property of the lithium secondary battery to produce and an elevated-temperature property are reduced at the time of charge and discharge. Then, the carbon material for negative electrodes with which it can improve and the lithium secondary battery of high capacity can produce a cycle property, an elevated-temperature property, and a rapid charge-and-discharge property is demanded.

[0005]

[Problem(s) to be Solved by the Invention] Invention according to claim 1 offers the manufacturing method of the suitable graphite particle for the lithium secondary battery negative-electrode carbon material of high capacity. In addition to the technical problem of invention according to claim 1, invention claims 2 and 3 and given in four offers the manufacturing method of the suitable graphite particle for the lithium secondary battery negative-electrode carbon material excellent in the cycle property and the elevated-temperature property. In addition to the technical problem of invention according to claim 1 to 4, invention according to claim 5 offers the manufacturing method of the suitable graphite particle for the negative-electrode carbon material for lithium secondary batteries excellent in the rapid charge-and-discharge property.

[0006] Invention according to claim 6 is high capacity, and offers the suitable graphite particle for the negative-electrode carbon material for lithium secondary batteries. In addition to the technical problem of invention according to claim 6, invention claim 7 and given in eight offers the suitable graphite particle for the carbon material for lithium secondary battery negative electrodes excellent in the cycle property and the elevated-temperature property. In addition to the technical problem of invention according to claim 6 to 8, invention according to claim 9 offers the suitable graphite particle for the negative-electrode carbon material for lithium secondary batteries excellent in the rapid charge-and-discharge property.

[0007] Invention according to claim 10 is high capacity, and offers the suitable negative-electrode carbon material for lithium secondary batteries for the lithium secondary battery excellent in the cycle property, the elevated-temperature property, and the rapid charge-and-discharge property. Invention according to claim 11 is high capacity, and offers the negative electrode for lithium secondary batteries excellent in the cycle property, the elevated-temperature property, and the rapid charge-and-discharge property. Invention according to claim 12 is high capacity, and offers the lithium secondary battery excellent in the cycle property, the elevated-temperature property, and the rapid charge-and-discharge property.

[0008]

[Means for Solving the Problem] This invention relates to the manufacturing method of the graphite particle characterized by including the process which calcinates and graphitizes the mixture containing the ingredient which can be graphitized, and at least two kinds of compounds containing a different metallic element. Moreover, this invention relates to the manufacturing method of the graphite particle which is the compound with which one kind contains B element among at least two kinds of compounds containing the metallic element from which the above differs.

[0009] Moreover, this invention relates to the manufacturing method of the graphite particle at least two kinds of whose compounds containing the metallic element from which the above differs are a compound containing B element, and a compound containing at least one kind of element of Fe, Si, nickel, and Ti. Moreover, this invention relates to the manufacturing method of the graphite particle which is 0.1 - 30 % of the weight in element conversion to the total

quantity of the ingredient which the amount of the compound which is 0.05 - 5 % of the weight in B element conversion, and contains at least one kind of element of Fe, Si, nickel, and Ti to the total quantity of the ingredient which the amount of the compound containing the aforementioned B element can graphitize, and the compound containing a metallic element can graphitize, and the compound containing a metallic element. Moreover, this invention relates to the manufacturing method of the graphite particle which is that in which the ingredient in which the aforementioned graphitization is possible contains the carbonaceous powder whose mean diameter is 1-50 micrometers, and the binder which can be graphitized. [0010] Moreover, this invention relates to the graphite particle containing at least two kinds of different metallic elements. Moreover, this invention relates to the graphite particle in which the aforementioned metallic element contains B element and at least one kind of element of Fe, Si, nickel, and Ti. Moreover, this invention relates to the graphite particle whose content of the aforementioned metallic element is 0.01 - 5 % of the weight. Moreover, this invention relates to the aforementioned graphite particle below 8m²/g and whose aspect ratio 10-100 micrometers and specific surface area are [the distance d between layers of a crystal (002) / the microcrystal size L_c (002) of 3.38Å or less and C shaft orientations] 1.1-5 for 500Å or more and mean particle diameter.

[0011] Moreover, this invention relates to the negative-electrode carbon material for lithium secondary batteries which consists of the graphite particle or the aforementioned graphite particle obtained according to the aforementioned manufacturing method. Moreover, this invention relates to the negative electrode for lithium secondary batteries which applies the aforementioned carbon material to a charge collector, and it comes to unify. Furthermore, this invention relates to the lithium secondary battery which comes to have the aforementioned negative electrode and a positive electrode containing a lithium compound.

[0012]

[Embodiment of the Invention] In this invention, the manufacturing method of the suitable graphite particle for the negative-electrode carbon material for lithium secondary batteries adds at least two kinds of compounds containing a metallic element which is different into the ingredient which can be graphitized, and is characterized by graphitizing through the process which calcinates the mixture. Thus, if at least two kinds of compounds containing a metallic element which is different into the ingredient which can be graphitized are added, in case the ingredient which can be graphitized is graphitized, these metallic elements will work as a graphitization catalyst, crystallinity will improve, and charge-and-discharge capacity will increase. Although this reason is not clear, the temperature fields where the catalyst effectiveness of a metallic element demonstrates the catalyst effectiveness according to the class of those elements differ, and since the temperature field which demonstrates the catalyst effectiveness becomes large by adding two or more kinds of metallic elements, a crystal is considered that it can advance development. Moreover, it is thought that the metallic element which demonstrates effectiveness by the elevated-temperature side among the metallic elements which are two kinds from which the temperature which demonstrates the catalyst effectiveness differs can make the effectiveness amplify by the metallic element which demonstrates the catalyst effectiveness by the low temperature side rather than it.

[0013] As a compound containing the metallic element to add, metals, such as B, Fe, Si, Ti, and nickel, those oxides, carbide, and a nitride are desirable in respect of the crystallinity of the graphite particle obtained. Furthermore, one kind in the compound containing two or more kinds of metallic elements to add has a desirable compound containing B element. Although many edges of a graphite crystal come to exist in a particle front face as a crystal progresses, although it can be made to progress highly by adding a catalyst, the crystallinity of the ingredient which

can be graphitized is adding the compound containing B element, and it becomes possible to control the amount of the edge of the graphite crystal on the front face of a particle, and to reduce specific surface area, and to raise crystallinity of it further. The edge of a graphite crystal can raise the cycle property and elevated-temperature property of a lithium secondary battery to produce by being easy to react with the electrolytic solution, and reducing the amount of the edge of a surface graphite crystal, since the reaction advances further at an elevated temperature. [0014] Moreover, as for the compound containing one more kind of metallic element, it is desirable that they are the compounds (an oxide, carbide, nitride, etc.) containing Fe, Si, Ti, or nickel. Thereby, a cycle property and an elevated-temperature property can be maintained and high capacity-ization can be attained.

[0015] As loadings of two or more kinds of compounds containing a different metallic element to add As opposed to the total quantity of the ingredient which can graphitize the compound containing B element although there is especially no limit, and the compound containing a metallic element Are desirable in respect of the irreversible capacity of the surface state of the negative-electrode carbon material using the graphite particle which 0.05 - 5% of the weight of the range produces by B element conversion, and the first cycle eye of the lithium secondary battery to produce. If it is 0.05 - 3% of the weight of the range, it is more desirable, and it is still more desirable if it is 0.05 - 1% of the weight of the range. The edge of a graphite crystal increases in the front face of the negative-electrode carbon material using the graphite particle which the compound containing B element produces by B element conversion as it is less than 0.05 % of the weight, and there is an inclination for the cycle property and elevated-temperature property of a lithium secondary battery which are produced as a result to fall. Moreover, when the compound containing B element exceeds 5 % of the weight by B element conversion, it is in the inclination for B element to tend to remain in the negative-electrode carbon material to produce, and for the irreversible capacity of the first cycle eye to become large by B which remained.

[0016] Moreover, 0.1 - 15% of the weight of the range is more desirable, and the addition of the compound containing at least one kind of element of Fe, Si, nickel, and Ti is still more desirable if it is 0.5 - 10% of the weight of the range, and especially if it is 0.5 - 5% of the weight of the range, it is desirable [0.1 - 30% of the weight of the range is desirable to the total quantity of the ingredient which can be graphitized, and the compound containing a metallic element at element conversion of each element and]. There is an inclination for the crystallinity of the graphite particle from which the addition of the compound containing at least one kind of element of Fe, Si, nickel, and Ti is obtained as it is less than 0.1 % of the weight in element conversion of each element to fall, and for the discharge capacity of a lithium secondary battery to fall. On the other hand, when it exceeds 30 % of the weight, the edge of a graphite crystal increases in the front face of the negative-electrode carbon material using the graphite particle obtained, and there is an inclination for the cycle property and elevated-temperature property of a lithium secondary battery to produce to fall.

[0017] As the mixed approach of of the two or more kinds of compounds and the ingredient which can be graphitized containing a different metallic element, there is nothing and you may mix with powder, and especially a limit may be mixed, after making a liquid fuse or distribute said compound.

[0018] As an ingredient which can be graphitized, although there is especially no limit, it is desirable that it is the ingredient with which a mean diameter contains 1-50-micrometer desirable carbonaceous powder and the desirable binder which can be graphitized. The rapid charge-and-discharge property of the lithium secondary battery which can make the aspect ratio of the graphite particle obtained small, consequently is produced by mixing the binder in which said

carbonaceous powder and graphitization are possible can be raised. As for the compound containing a metallic element, it is desirable to add, in case the binder which can be graphitized is mixed with carbonaceous powder, and to mix to coincidence. As for the temperature to mix, it is desirable that it is the temperature in which the binder which can be graphitized carries out softening fusion, and although the temperature changes with ingredients to be used, the range of 50-350 degrees C is desirable. Moreover, with a solvent etc., when using as a solution the binder which can be graphitized, it may be mixed in ordinary temperature.

[0019] As carbonaceous powder, graphite powder, such as carbide of resin, natural-graphite powder, and artificial-graphite powder, can be used in the end of a coke breeze, such as needle coke, for example. As a binder which can be graphitized, organic system ingredients, such as thermosetting resin besides being a pitch, tar, etc. and thermoplastics, are raised.

[0020] As for the graphite precursor which mixed two or more kinds of compounds containing a metallic element with the ingredient which can be graphitized, like the above, it is desirable to calcinate and graphitize at the temperature of 2500 degrees C or more. In this invention, before graphitizing this graphite precursor at the temperature of 2500 degrees C or more, grinding and shaping may be performed and you may calcinate at the temperature of about further 700-1300 degrees C. Moreover, after calcinating at the temperature of about 700-1300 degrees C, grinding and adjusting grain size, you may calcinate and graphitize at the temperature of 2500 degrees C or more by fine particles. In respect of the crystallinity of the negative-electrode carbon material obtained, and discharge capacity, 2500 degrees C or more are desirable, and the burning temperature at the time of graphitization is more desirable if it is 2800 degrees C or more, and if it is 3000 degrees C or more, it is still more desirable. If the ambient atmospheres at the time of baking are the conditions which cannot oxidize easily, there will be especially no limit, for example, nitrogen-gas-atmosphere mind, an argon ambient atmosphere, and the vacuum middle class will be mentioned.

[0021] Subsequently, although it grinds, and grain size is adjusted and being considered as a graphite particle, as the grinding approach, there is especially no limit, for example, it can take impact crushing methods, such as a jet mill, a hammer mill, and a pin mill. Especially the mean particle diameter of the graphite particle after grinding has desirable 10-50 micrometers 10-100 micrometers. However, when it grinds before graphitization and grain size is adjusted, it is not necessary to grind after graphitization. In addition, in this invention, mean particle diameter can be measured with a laser diffraction type particle-size-distribution meter.

[0022] Although the graphite particle produced as mentioned above comes to contain two or more kinds of metallic elements in the graphite particle, as for the content, it is desirable that it is 0.01 - 5 % of the weight. When it exceeds 5 % of the weight, it is in the inclination for there to be an inclination for the irreversible capacity of the first cycle eye of the lithium secondary battery to produce to become large, and for the self-discharge property of a lithium secondary battery to fall.

[0023] Moreover, since the lithium secondary battery with which 500A or more and mean particle diameter are [micrometers / 10-100 / and specific surface area] high capacity as it is that below 8m²/g and whose aspect ratio are 1.1-5, and the distance d between layers of a crystal (002) excelled [size / Lc (002) / ofA / 3.38 / or less / and C shaft orientations / microcrystal] in the cycle property, the elevated-temperature property, and the rapid charge-and-discharge property is obtained, the graphite particle obtained is desirable.

[0024] The distance d between layers of a crystal (002) is a value in the X-ray wide angle diffraction of a graphite particle, and when this value exceeds 3.38A, it has the inclination for discharge capacity to become small here. Moreover, the microcrystal size Lc (002) of C shaft orientations is also a value in the X-ray wide angle diffraction of a graphite particle, and has the

inclination for discharge capacity to become it small that this value is less than 500A. Moreover, less than by 1.1, an aspect ratio is in the inclination for conductivity to fall, when the touch area between particles decreases. On the other hand, when the aspect ratio of a graphite particle becomes larger than 5, there is an inclination to become easy for a rapid charge-and-discharge property to fall. In addition, an aspect ratio is expressed with A/B, when major-axis lay length of a graphite particle is set to A and it sets minor-axis lay length to B. The aspect ratio in this invention expands a graphite particle under a microscope, chooses 100 graphite particles as arbitration, measures A/B, and takes the average.

[0025] Moreover, when the specific surface area of a graphite particle exceeds 8m²/g, the irreversible capacity of the first cycle eye of the lithium secondary battery obtained becomes large, energy density is small, and in case a negative electrode is produced further, there is a problem that many binders are needed. Measurement of specific surface area can take known approaches, such as a BET adsorption method (nitrogen gas absorption method). And it is mean particle diameter, the graphite particle obtained has desirable 10-100 micrometers, and its 10-50 micrometers are more desirable.

[0026] The graphite particle obtained as mentioned above can be used as a negative-electrode ingredient for lithium secondary batteries of this invention as it is.

[0027] The negative-electrode carbon material for lithium secondary batteries which becomes this invention is kneaded with an organic system binder and a solvent, is made into the shape of a paste, and can be fabricated in configurations, such as the shape of a sheet, and a pellet type. As an organic system binder, polyethylene, polypropylene, ethylene-propylene terpolymer, butadiene rubber, styrene butadiene rubber, isobutylene isoprene rubber, a high molecular compound with big ionic conductivity, etc. can be used, for example.

[0028] As a high molecular compound with said big ionic conductivity, polyvinylidene fluoride, polyethylene oxide, polyepichlorohydrin, poly FASUFAZEN, a polyacrylonitrile, etc. can be used. the mixing ratio of a carbon material and an organic system binder -- a rate -- the carbon material 100 weight section -- receiving -- an organic system binder -- **** for 1 - 20 weight sections -- things are desirable.

[0029] As said solvent, there is especially no limit and a N-methyl-2-pyrrolidone, dimethylformamide, isopropanol, etc. are raised. Especially a limit does not have the amount of a solvent, either, and after it kneads a carbon material with an organic system binder and a solvent and it adjusts viscosity, it applies to a charge collector, it unites with this charge collector, and let it be a negative electrode. As a charge collector, metal charge collectors, such as foils, such as nickel and copper, and a mesh, can be used, for example. In addition, unification can be performed by the fabricating methods, such as a roll and a press, and you may unify combining these.

[0030] Thus, the obtained negative electrode is used for the lithium secondary battery of this invention with the positive electrode containing a lithium compound. It can obtain by a lithium secondary battery's countering and arranging a positive electrode and a negative electrode through a separator, and pouring in the electrolytic solution, and this is excellent in a cycle property, an elevated-temperature property, and a rapid charge-and-discharge property with high capacity as compared with the lithium secondary battery which used the conventional carbon material for the negative electrode.
 [0031] there is especially no limit in the ingredient, for example, independent in LiNiO₂, LiCoO₂, and LiMn₂O₄ grade, although the positive electrode of the lithium secondary battery in this invention contains a lithium compound -- or it can be mixed and used. The lithium secondary battery in this invention contains the electrolytic solution which usually contains a lithium compound with a positive electrode and a negative electrode.

[0032] As the electrolytic solution, the so-called organic electrolytic solution which melted the

lithium salt of LiClO_4 , LiPF_6 , LiAsF_6 , LiBF_4 , and LiSO_3CF_3 grade to nonaqueous solvents, such as ethylene carbonate, diethyl carbonate, dimethoxyethane, dimethyl carbonate, methylethyl carbonate, and a tetrahydrofuran, and a solid-state or the so-called gel polymer electrolyte can be used.

[0033] the nonwoven fabric which used polyolefines, such as polyethylene and polypropylene, as the principal component as a separator, for example, a cross, and a fine hole -- what combined a film or them can be used. In addition, when the positive electrode and negative electrode of the lithium secondary battery to produce make it the structure where it does not contact directly, it is not necessary to use a separator.

[0034] in addition, drawing 1 -- a part of example of a cylindrical lithium secondary battery -- a cross-section front view is shown. The positive electrode 1 processed in the shape of sheet metal and the negative electrode 2 processed similarly wind what was piled up through the separators 3, such as a micropore film made from polyethylene, and the cylindrical lithium secondary battery shown in drawing 1 inserts this in the cell cans 7, such as metal, and is sealing-ized. A positive electrode 1 is joined to the positive-electrode lid 6 through the positive-electrode tab 4, and the negative electrode 2 is joined to the cell pars basilaris ossis occipitalis through the negative-electrode tab 5. The positive-electrode lid 6 is being fixed to the cell can (positive-electrode can) 7 with the gasket 8.

[0035]

[Example] Hereafter, the example of this invention is explained.

One weight section (it is the 0.175 weight section by B element conversion) and the iron-oxide 5 weight section (they are the 3.5 weight sections by Fe element conversion) were mixed for 50 weight sections, the pitch 15 weight section, the coal tar 10 weight section, and a way acid at 230 degrees C for 1 hour in the coke breeze end of 10 micrometers of example 1 mean diameters. Subsequently, this mixture was ground in mean particle diameter of 25 micrometers, press forming of this grinding object was put in and carried out to metal mold, and it fabricated in the rectangular parallelepiped. After heat-treating this Plastic solid at 1000 degrees C in nitrogen-gas-atmosphere mind, it heat-treated at 3000 degrees C in nitrogen-gas-atmosphere mind further, and the graphite Plastic solid was acquired. Furthermore this graphite Plastic solid was pulverized and it considered as the graphite particle. The measured value of the mean particle diameter of the obtained graphite particle, $d(002)$ and $L_c(002)$, specific surface area, an aspect ratio, and ash content (the amount of metal survival) is shown in Table 1.

[0036] Subsequently, as it was, the polyvinylidene fluoride (PVDF) dissolved in 90 % of the weight of this negative-electrode carbon material at the N-methyl-2-pyrrolidone was added 10% of the weight, was kneaded by solid content, by having used the obtained graphite particle as the negative-electrode carbon material, and the graphite paste was produced. Thickness applied and carried out the vacuum drying of this graphite paste to the rolling copper foil which is 10 micrometers, and it considered as the test electrode.

[0037] Constant current charge and discharge according the produced sample electrode to 3 terminal method were performed, and charge-and-discharge capacity was measured. Evaluation of a sample electrode put the solution which dissolved LiPF_6 so that it might become to the concentration of one mol/l. at the mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC and DEC are 1:1 at a volume ratio) as the electrolytic solution 10 into the glass beaker mold cel 9, as shown in drawing 2, the laminating of a sample electrode 11, a separator 12, and the counter electrode 13 was carried out, and it has arranged them, hung the reference pole 14 from the upper part further, and produced the model cell. In addition, the metal lithium was used for the counter electrode 13 and the reference pole 14, and the polyethylene micropore film was used for the separator 4. Using the obtained model cell, between the sample

electrode 11 and the counter electrode 13, it charged to 0V (V vs. Li/Li+) by the constant current of 0.3 mA/cm² to the area of a sample electrode, and the trial which discharges to 1V (V vs. Li/Li+) was performed. The discharge capacity and irreversible capacity per unit weight of 1 cycle eye of a negative-electrode carbon material are shown in Table 1.

[0038] Subsequently, the lithium secondary battery was produced using the obtained negative-electrode carbon material. It is the following, and the lithium secondary battery of this invention shown in drawing 1 was made and produced. as positive active material -- LiCoO₂ 88 % of the weight -- using -- as an electric conduction agent -- the scale-like graphite of 2 micrometers of mean diameters -- as 7 % of the weight and a binder -- 5 % of the weight (PVDF) of polyvinylidene fluorides -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a positive electrode -- the paste of a mixture was adjusted.

[0039] the negative-electrode carbon material similarly produced by the aforementioned approach as a negative-electrode active material -- as a binder -- PVDF -- 10 % of the weight -- adding -- this -- a N-methyl-2-pyrrolidone -- adding -- mixing -- a negative electrode -- the paste of a mixture was adjusted. a positive electrode -- after making the mixture into both sides of aluminium foil with a thickness of 25 micrometers with ** and carrying out a vacuum drying at 120 degrees C after that for 1 hour, by the roll press, pressing of the electrode was carried out, it started further in with a width die length [285mm die length of 40mm] magnitude, and the positive electrode was produced. however, a part with a die length [of the both ends of a positive electrode] of 10mm -- a positive electrode -- a mixture was not applied, but aluminium foil is exposed, and the positive-electrode tab is stuck to one of these by pressure by ultrasonic jointing.

[0040] on the other hand -- a negative electrode -- the mixture was applied to both sides of copper foil with a thickness of 10 micrometers, and carried out the vacuum drying at 120 degrees C after that for 1 hour. After the vacuum drying, by the roll press, pressing of the electrode was carried out, it started further in with a width die length [290mm die length of 40mm] magnitude, and the negative electrode was produced. a positive electrode -- the same -- a part with a die length [of the both ends of a negative electrode] of 10mm -- a negative electrode -- a mixture was not applied, but copper foil was exposed, and the negative-electrode tab was stuck to one of these by pressure by ultrasonic jointing.

[0041] The with a thickness width [44mm width of 25 micrometers] micropore film made from polyethylene was used for the separator. Superposition and this were wound in order of the positive electrode, the separator, the negative electrode, and the separator, and it considered as the electrode group. this -- AA -- it inserted in the cell can of size, can bottom welding of the negative-electrode tab was carried out, and the converging section for closing a positive-electrode lid was formed. After the volume ratio poured into the cell can the electrolytic solution made to dissolve one mol /of 6 phosphorus-fluoride acid lithiums in the mixed solvent of the ethylene carbonate and diethyl carbonate of 1:1 l. and welding a positive-electrode tab to a positive-electrode lid, the positive-electrode lid was closed and the cell was produced. Charge and discharge were repeated for 300mA of charge and discharge currents, and a charge-and-discharge termination electrical potential difference at 45 degrees C as 4.2V and 2.8V using this cell, respectively. The measurement result of 45-degree-C cycle property is shown in drawing 3 .

[0042] Ten weight sections (it is the 1.75 weight section by B element conversion) and the iron-oxide 10 weight section (they are 7 weight sections by Fe element conversion) were mixed for 50 weight sections, the pitch 15 weight section, the coal tar 10 weight section, and a way acid at 230 degrees C for 1 hour in the coke breeze end of 10 micrometers of example 2 mean diameters. Subsequently, this mixture was ground in mean particle diameter of 25 micrometers, press

forming of this grinding object was put in and carried out to metal mold, and it fabricated in the rectangular parallelepiped. After heat-treating this Plastic solid at 1000 degrees C in nitrogen-gas-atmosphere mind, it heat-treated at 3000 degrees C in nitrogen-gas-atmosphere mind further, and the graphite Plastic solid was acquired. Furthermore this graphite Plastic solid was pulverized and it considered as the graphite particle. The measured value of the discharge capacity per carbon unit weight of the mean particle diameter which measured this negative-electrode carbon material by the same approach as an example 1, d (002) and Lc (002), specific surface area, an aspect ratio and ash content, and 1 cycle eye, and irreversible capacity is shown in Table 1, using the obtained graphite particle as a negative-electrode carbon material as it is. moreover, the approach as an example 1 that it is the same except having used said negative-electrode carbon material for the negative electrode -- AA -- the lithium secondary battery of size was produced and the cycle property in 45 degrees C was measured like the example 1. The result is shown in drawing 3 .

[0043] The graphite particle produced in the example 3 example 2 was heat-treated at 2600 degrees C in the vacuum, and the graphite particle was obtained. The measured value of the discharge capacity per carbon unit weight of the mean particle diameter measured by the same approach as an example 1, d (002) and Lc (002), specific surface area, an aspect ratio and ash content, and 1 cycle eye and irreversible capacity is shown in Table 1 by using the obtained graphite particle as a negative-electrode carbon material. moreover, the approach as an example 1 that it is the same except having used said negative-electrode carbon material for the negative electrode -- AA -- the lithium secondary battery of size was produced and the cycle property in 45 degrees C was measured like the example 1. The result is shown in drawing 3 .

[0044] The 0.5 weight section (it is the 0.0875 weight section by B element conversion) and the silicon carbide 25 weight section (they are the 17.8 weight sections by Si element conversion) were mixed for 50 weight sections, the pitch 15 weight section, the coal tar 10 weight section, and a way acid at 230 degrees C for 1 hour in the coke breeze end of 10 micrometers of example 4 mean diameters. Subsequently, this mixture was ground in mean particle diameter of 25 micrometers, press forming of this grinding object was put in and carried out to metal mold, and it fabricated in the rectangular parallelepiped. After heat-treating this Plastic solid at 1000 degrees C in nitrogen-gas-atmosphere mind, it heat-treated at 3000 degrees C in nitrogen-gas-atmosphere mind further, and the graphite Plastic solid was acquired. Furthermore this graphite Plastic solid was pulverized and it considered as the graphite particle. The measured value of the discharge capacity per carbon unit weight of the mean particle diameter which measured this negative-electrode carbon material by the same approach as an example 1, d (002) and Lc (002), specific surface area, an aspect ratio and ash content, and 1 cycle eye, and irreversible capacity is shown in Table 1 by using the obtained graphite particle as a negative-electrode carbon material. moreover, the approach as an example 1 that it is the same except having used said negative-electrode carbon material for the negative electrode -- AA -- the lithium secondary battery of size was produced and the cycle property in 45 degrees C was measured like the example 1. The result is shown in drawing 3 .

[0045] Ten weight sections (it is the 1.75 weight section by B element conversion) were mixed for 50 weight sections, the pitch 15 weight section, the coal tar 10 weight section, and a way acid at 230 degrees C for 1 hour in the coke breeze end of 10 micrometers of example of comparison 1 mean diameters. Subsequently, this mixture was ground in mean particle diameter of 25 micrometers, press forming of this grinding object was put in and carried out to metal mold, and it fabricated in the rectangular parallelepiped. After heat-treating this Plastic solid at 1000 degrees C in nitrogen-gas-atmosphere mind, it heat-treated at 3000 degrees C in nitrogen-gas-atmosphere mind further, and the graphite Plastic solid was acquired. Furthermore this graphite

Plastic solid was pulverized and it considered as the graphite particle. The measured value of the discharge capacity per carbon unit weight of the mean particle diameter which measured this negative-electrode carbon material by the same approach as an example 1, d (002) and Lc (002), specific surface area, an aspect ratio and ash content, and 1 cycle eye, and irreversible capacity is shown in Table 1 by using the obtained graphite particle as a negative-electrode carbon material. moreover, the approach as an example 1 that it is the same except having used said negative-electrode carbon material for the negative electrode -- AA -- the lithium secondary battery of size was produced and the cycle property in 45 degrees C was measured like the example 1. The result is shown in drawing 3 .

[0046] 50 weight sections, the pitch 15 weight section, the coal tar 10 weight section, and the iron-oxide 5 weight section (they are the 3.5 weight sections by Fe element conversion) were mixed at 230 degrees C for 1 hour in the coke breeze end of 10 micrometers of example of comparison 2 mean diameters. Subsequently, this mixture was ground in mean particle diameter of 25 micrometers, press forming of this grinding object was put in and carried out to metal mold, and it fabricated in the rectangular parallelepiped. After heat-treating this Plastic solid at 1000 degrees C in nitrogen-gas-atmosphere mind, it heat-treated at 3000 degrees C in nitrogen-gas-atmosphere mind further, and the graphite Plastic solid was acquired. Furthermore this graphite Plastic solid was pulverized and it considered as the graphite particle. The measured value of the discharge capacity per carbon unit weight of the mean particle diameter which measured this negative-electrode carbon material by the same approach as an example 1, d (002) and Lc (002), specific surface area, an aspect ratio and ash content, and 1 cycle eye, and irreversible capacity is shown in Table 1 by using the obtained graphite particle as a negative-electrode carbon material. moreover, the approach as an example 1 that it is the same except having used said negative-electrode carbon material for the negative electrode -- AA -- the lithium secondary battery of size was produced and the cycle property in 45 degrees C was measured like the example 1. The result is shown in drawing 3 .

[0047] 50 weight sections, the pitch 15 weight section, the coal tar 10 weight section, and the silicon carbide 25 weight section (they are the 17.8 weight sections by Si element conversion) were mixed at 230 degrees C for 1 hour in the coke breeze end of 10 micrometers of example of comparison 3 mean diameters. Subsequently, this mixture was ground in mean particle diameter of 25 micrometers, press forming of this grinding object was put in and carried out to metal mold, and it fabricated in the rectangular parallelepiped. After heat-treating this Plastic solid at 1000 degrees C in nitrogen-gas-atmosphere mind, it heat-treated at 3000 degrees C in nitrogen-gas-atmosphere mind further, and the graphite Plastic solid was acquired. Furthermore this graphite Plastic solid was pulverized and it considered as the graphite particle. The measured value of the discharge capacity per carbon unit weight of the mean particle diameter which measured this negative-electrode carbon material by the same approach as an example 1, d (002) and Lc (002), specific surface area, an aspect ratio and ash content, and 1 cycle eye, and irreversible capacity is shown in Table 1 by using the obtained graphite particle as a negative-electrode carbon material. moreover, the approach as an example 1 that it is the same except having used said negative-electrode carbon material for the negative electrode -- AA -- the lithium secondary battery of size was produced and the cycle property in 45 degrees C was measured like the example 1. The result is shown in drawing 3 .

[0048]

[Table 1]

表 1

	実施例 1	実施例 2	実施例 3	実施例 4	比較例 1	比較例 2	比較例 3
平均粒径 (μm)	25.2	27.5	27.0	22.0	24.3	23.6	21.8
d(002) (Å)	3.359	3.354	3.354	3.355	3.359	3.360	3.355
Lc(002) (Å)	943	>1000	>1000	>1000	825	950	>1000
比表面積 (m^2/g)	3.3	2.7	2.0	2.9	3.2	4.1	3.0
アスペクト比	1.7	1.6	2.5	2.6	1.5	2.1	3.5
灰分 (%)	0.11	1.60	0.01	0.08	1.42	0.01	0.01
放電容量 (mAh/g)	336	342	350	355	327	335	350
不可逆容量 (mAh/g)	28	38	25	29	39	46	38

[0049] As shown in Table 1 and drawing 3, the carbon material for negative electrodes of this invention is high capacity, and it was shown that it is suitable as a lithium secondary battery excellent in the elevated-temperature cycle property.

[0050]

[Effect of the Invention] According to the manufacturing method of a graphite particle according to claim 1, the suitable graphite particle for the lithium secondary battery carbon material of high capacity is obtained. According to the manufacturing method of claims 2 and 3 and a graphite particle given in four, an effect of the invention according to claim 1 is done so, and the suitable graphite particle for the lithium secondary battery negative-electrode carbon material which was further excellent in the cycle property and the elevated-temperature property is obtained.

According to the manufacturing method of a graphite particle according to claim 5, an effect of the invention according to claim 1 to 4 is done so, and the suitable graphite particle for the lithium secondary battery negative-electrode carbon material which was further excellent in the rapid charge-and-discharge property is obtained.

[0051] As a negative-electrode carbon material, a graphite particle according to claim 6 is high capacity, and suitable for a lithium secondary battery. Claim 7 and a graphite particle given in eight do so an effect of the invention according to claim 6, and are still more suitable as a negative-electrode carbon material of the lithium secondary battery excellent in the cycle property and the elevated-temperature property. A graphite particle according to claim 9 does so an effect of the invention according to claim 6 to 8, and is still more suitable as an amount of negative-electrode material of the lithium secondary battery excellent in the rapid charge-and-discharge property.

[0052] The negative-electrode carbon material for lithium secondary batteries according to claim 10 is high capacity, and excellent in a cycle property, an elevated-temperature property, and a rapid charge-and-discharge property. The negative electrode for lithium secondary batteries according to claim 11 is high capacity, and excellent in a cycle property, an elevated-temperature property, and a rapid charge-and-discharge property. A lithium secondary battery according to claim 12 is high capacity, and excellent in a cycle property, an elevated-temperature property, and a rapid charge-and-discharge property.

[Translation done.]

Knovel Solvents - A Properties Database

Display: Data Found All Data

Table: Physical & Chemical Properties






Table Type: Interactive Table

Search Query: (cyclohexane) AND (density)

Data Found (Search): 6 rows retrieved out of 1141 rows

Number of Hidden Columns: 2

Select Rows Find Data Filter Data A-Z Sort Z-A Table Show/Hide Columns Change Order Print Table Export Table View Table Notes Back to Search Results Unit Conve

	no.	material or substance name	synonym	chemical category	composition	molecular formula	structure	mol. weight	CAS Registry No.	UN No.	RTECS No.	state	color
	A-Z												
<input type="checkbox"/>	154	sec-Butylcyclohexane	(1-methylpropyl)-1-cyclohexane	Aliphatic Hydrocarbons		C ₁₀ H ₂₀		140.27	52993-54-1			Liquid	colorless
<input type="checkbox"/>	225	Cyclohexane	hexamethylene; hexahydrobenzene	Aliphatic Hydrocarbons		C ₆ H ₁₂		84.2	110-82-7	1145	GU6300000	Liquid	colorless
<input type="checkbox"/>	472	Ethyl cyclohexane		Aliphatic Hydrocarbons		C ₈ H ₁₆		112.2	1678-91-7			Liquid	
<input type="checkbox"/>	637	Isobutyl cyclohexane		Aliphatic Hydrocarbons		C ₁₀ H ₂₀		147.27	1678-98-4			Liquid	colorless
<input type="checkbox"/>	920	Shell Hexane (extraction grade)		Aliphatic Hydrocarbons	n-hexane - 50 wt%, cyclohexane - 3 wt%, C6 total >98 wt%, aromatics - 0.001 wt%, benzene <10 mg				64742-49-0			Liquid	
<input type="checkbox"/>	922	Shell Hexane Polymerization Grade	n-hexane	Aliphatic Hydrocarbons	aromatics <0.01 wt%, n-hexane >40 wt%, cyclohexane <3 wt%, sulfur <1 mg/kg, water <100 mg	C ₆ H ₁₄						Liquid	